

Ewald sums for Yukawa potentials in quasi-two-dimensional systems.

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Abstract

In this note, we derive Ewald sums for Yukawa potential for three dimensional systems with two dimensional periodicity. This sums are derived from the Ewald sums for Yukawa potentials with three dimensional periodicity [G. Salin and J.-M. Caillol, *J. Chem. Phys.* **113**, 10459 (2000)] by using the method proposed by Parry for the Coulomb interactions [D.E. Parry, *Surf. Sci.* **49**, 433 (1975); **54**, 195 (1976)].

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The Yukawa interaction energy between two particles is given by

$$E(r) = \frac{y_i y_j}{\epsilon} \frac{\exp(-\kappa r)}{r} \quad (1)$$

where ϵ is the dielectric constant, κ the inverse of the screening length and y_i the "Yukawa charges" defined by the properties and the state of the system ; for instance, at the Debye-Hückel approximation for electrolytes or in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloids, κ and y_i are related to physical parameters of systems as

$$\kappa = \sqrt{\frac{q^2 \rho}{k_B T \epsilon}} \quad \text{and} \quad y_i = \frac{q \exp(\kappa \sigma_i)}{(1 + \kappa \sigma_i)}$$

where σ_i is the diameter of the hard core of the ions, in the Debye-Hückel approximations, or the radius of macroions, in DLVO theory, and ρ and q are respectively the density of ions or counterions and their charge, k_B the Boltzmann constant and T the temperature. Yukawa interactions between particles are used in numerical simulations as effective potentials to simulate systems as plasmas, dusty plasma, colloids, etc. ; on general ground, such potentials may be used as a reasonable approximation, as soon as some microscopic degrees of freedom may be approximated to a continuous background leading to a screening of the direct interaction between particles, while the spherical symmetry of the interaction is preserved.

As outlined in ref.[1], if κ is large enough, the screening length can be much smaller than simulation box lengths, then interactions between particles are not long ranged and, in practice, a simple truncation of the potential, with the use of the minimum image convention, could be sufficient. On the contrary, if κ is not large or quite small, then interactions between particles may be long ranged and images of particles introduced by the periodic boundary conditions may contribute significantly to the energy of the system. In these cases, a crude truncation of the potential could lead to strong bias in computations (for Coulomb interactions, see for instance refs.[2-4] for errors introduced by crude truncations of long ranged potentials). To handle these latter cases, an Ewald method for systems with

three dimensional periodicity and Yukawa interaction potentials has been exhibited¹.

Many interesting systems which interaction between particles can be approximated by Yukawa potentials are also confined to quasi-two dimensional geometries^{5,6,7}, therefore an Ewald method is of interest to permit to simulate the properties of these quasi-two dimensional systems for any value of the κ parameter including at low counterions concentration or high temperatures.

In this note, we derive Ewald sums for Yukawa potential in quasi-two dimensional systems from results of ref.[1] following the same derivation done by Parry⁸ for Coulomb interactions. For Coulomb interaction in quasi-two dimensional systems several methods exist^{9,10}, in particular some methods used the Ewald method for three dimensional systems with a highly asymmetric box^{11,12} and by adding correction terms related to the total dipole of the simulation box ; a general review on Coulomb interaction in quasi two-dimensional systems is done in ref.[10]. In a forthcoming work, some numerical implementations on a test system will be given ; the present work is devoted only to provide a simple derivation of Ewald sums for Yukawa potential in quasi-two dimensional systems.

As computed by Salin and Caillol¹, the Ewald-Yukawa interaction energy is given by

$$E = E_{\mathbf{r}} + E_{\mathbf{k}} - E_{\text{Self}} \quad (2)$$

with the short ranged contribution

$$E_{\mathbf{r}} = \frac{1}{4} \sum_{ij} \sum'_{\mathbf{n}} y_i y_j \frac{D(r_{ij}, \mathbf{n}, \kappa; \alpha)}{|\mathbf{r}_{ij} + \mathbf{nL}|} \quad (3)$$

where

$$\begin{aligned} D(r_{ij}, \mathbf{n}, \kappa; \alpha) &= \text{erfc}(\alpha |\mathbf{r}_{ij} + \mathbf{nL}| + \frac{\kappa}{2\alpha}) \exp(\kappa |\mathbf{r}_{ij} + \mathbf{nL}|) \\ &+ \text{erfc}(\alpha |\mathbf{r}_{ij} + \mathbf{nL}| - \frac{\kappa}{2\alpha}) \exp(-\kappa |\mathbf{r}_{ij} + \mathbf{nL}|) \end{aligned} \quad (4)$$

and r_{ij} the distance between the pair (i, j) of particles, the long ranged contribution

$$E_{\mathbf{k}} = \frac{2\pi}{V} \sum_{\mathbf{k} \neq 0} \frac{\exp(-\mathbf{k}^2 + \kappa^2)/4\alpha^2}{\mathbf{k}^2 + \kappa^2} \left| \sum_i y_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right|^2 \quad (5)$$

and the self interaction

$$E_{\text{Self}} = \left[\frac{\alpha}{\sqrt{\pi}} \exp\left(-\frac{\kappa^2}{4\alpha^2}\right) - \frac{\kappa}{2} \operatorname{erfc}\left(\frac{\kappa}{2\alpha}\right) \right] \sum_i y_i^2 \quad (6)$$

where we have set $\epsilon = 1$ and used conventional notations for Ewald sums ; namely, V is the volume of the simulation box, \mathbf{nL} the condensed notation for the vectors of the periodic boundary conditions, \mathbf{k} are the vectors belonging to the reciprocal lattice associated with the three dimensional periodicity and α the damping parameter of the Ewald method. In Eq.(3), the prime in the sum over \mathbf{n} indicates that for $\mathbf{n} = 0$, the self terms $i = j$ are not included. The short ranged contributions for the Ewald sums for Yukawa potentials in periodic three dimensional systems are given as in Eq.(3), for quasi-two dimensional⁸ the short ranged contributions are also given by Eq.(3) ; for practical applications, a choice of the Ewald damping parameter α is done such that summations over images are restricted to the minimum image convention¹.

In the work by Parry⁸, the Ewald sums for quasi-two dimensional systems are derived from the Ewald method for three dimensional systems by letting the spatial periodicity along the third direction to tend to infinity ($L_z \rightarrow \infty$).

In the following, we use the notations $\mathbf{k} = \mathbf{G} + k\mathbf{e}_z$ where \mathbf{G} are the vectors belonging to the reciprocal lattice associated with the two dimensional periodicity and $k = 2\pi m/L_z$, (m integer), where L_z is the spatial periodicity of the simulation box along the \mathbf{e}_z ; we set also $\mathbf{r}_{ij} = \mathbf{s}_{ij} + z_{ij}\mathbf{e}_z$ and $V = AL_z$, where s_{ij} is the distance in the plane perpendicular to \mathbf{e}_z and A is the surface of the simulation box for quasi-two dimensional systems.

Following Parry⁸, the long ranged contribution is separated into two contributions. The first contribution^{8(a)}, noted $E_{G \neq 0}^{(a)}$, is obtained for $\mathbf{G} \neq 0$ and the second^{8(b)} for $\mathbf{G} = 0$, as a reminiscent contribution of summation over k as $L_z \rightarrow \infty$, noted below $E_{G=0}^{(b)}$.

From Eq.(5), we have

$$\begin{aligned} E_{G \neq 0}^{(a)} &= \frac{2\pi}{A} \sum_{ij} y_i y_j \sum_{\mathbf{G} \neq 0} \exp(i\mathbf{G} \cdot \mathbf{s}_{ij}) \exp(-(\mathbf{G}^2 + \kappa^2)/4\alpha^2) \\ &\times \lim_{L_z \rightarrow \infty} \frac{1}{L_z} \sum_{r=-\infty}^{+\infty} \frac{\exp(-k^2/4\alpha^2)}{k^2 + (\mathbf{G}^2 + \kappa^2)} \exp(ikz_{ij}) \end{aligned} \quad (7)$$

Taking into account the identity¹³

$$\lim_{L \rightarrow \infty} \frac{1}{L} \sum_{r=-\infty}^{+\infty} \frac{\exp(-k^2/4\alpha^2)}{k^2 + (\mathbf{G}^2 + \kappa^2)} \exp(ikz_{ij}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk \frac{\exp(ikz) \exp(-k^2/4\alpha^2)}{k^2 + (\mathbf{G}^2 + \kappa^2)} \quad (8)$$

we found

$$E_{G \neq 0}^{(a)} = \frac{\pi}{2A} \sum_{\mathbf{G} \neq 0} \sum_{ij} y_i y_j F(\sqrt{\mathbf{G}^2 + \kappa^2}, z_{ij}; \alpha) \exp(i\mathbf{G} \cdot \mathbf{s}_{ij}) \quad (9)$$

with

$$F(K, z; \alpha) = \frac{1}{K} \left(\exp(Kz) \operatorname{erfc}\left(\frac{K}{2\alpha} + \alpha z\right) + \exp(-Kz) \operatorname{erfc}\left(\frac{K}{2\alpha} - \alpha z\right) \right) \quad (10)$$

The second contribution is given by

$$E_{G=0}^{(b)} = \frac{\pi}{2A} \sum_{ij} y_i y_j F(\kappa, z_{ij}; \alpha) \quad (11)$$

As it is shown explicitly on Eqs.(9) and (11), the long ranged contributions of Ewald-Yukawa sums for quasi-two dimensional systems can not be reduced to one particle summation, because of the complicated dependence on z_{ij} .

Self energy is given by

$$\begin{cases} E^{Q2D}(\text{Self}) &= \left[\frac{\alpha}{\sqrt{\pi}} \exp(-\kappa^2/4\alpha^2) - \frac{\kappa}{2} \operatorname{erfc}(\kappa/2\alpha) \right] \sum_i y_i^2 \\ E_{G=0}(\text{Self}) &= \frac{\pi}{A} \frac{\operatorname{erfc}(\kappa/2\alpha)}{\kappa} \sum_i y_i^2 \end{cases} \quad (12)$$

The Ewald sums for Yukawa potential in quasi-two dimensional systems are given by

$$E = E_{\mathbf{r}} + E_{G \neq 0}^{(a)} + E_{G=0}^{(b)} - E^{Q2D}(\text{Self}) - E_{G=0}(\text{Self}) \quad (13)$$

with each contribution given by Eqs.(3,9,11) and (12).

When $\kappa \rightarrow 0$, the Helmholtz equation, which solutions lead to Yukawa potentials, becomes a Poisson equation, which solutions lead to Coulomb potentials¹; then the Ewald sums for Coulomb interactions may be recovered from Eqs.(3,9,11) and (12), under the condition that the electroneutrality of the periodic system is recovered too^{14,15} (for instance by

letting the counterions concentration acting as an uniform continuous background).

When $z_{ij} = 0$ for all pairs of particles, then all particles are confined in a plan. In this limit, the Ewald sums for a quasi-two dimensional systems reduce to the Ewald sums of two dimensional systems. Then, Eqs.(9,12) and (13) become

$$E^{2D} = E_{\mathbf{s}} + E_{G \neq 0} - E_{\text{Self}}^{2D} \quad (14)$$

with

$$\left\{ \begin{array}{l} E_{G \neq 0} = \frac{\pi}{A} \sum_{\mathbf{G} \neq 0} \frac{\operatorname{erfc}(\sqrt{\mathbf{G}^2 + \kappa^2}/2\alpha)}{\sqrt{\mathbf{G}^2 + \kappa^2}} \left| \sum_i y_i \exp(i\mathbf{G} \cdot \mathbf{s}_i) \right|^2 \\ E_{\text{Self}}^{2D} = \left[\frac{\alpha}{\sqrt{\pi}} \exp(-\kappa^2/4\alpha^2) - \frac{\kappa}{2} \operatorname{erfc}(\kappa/2\alpha) \right] \sum_i y_i^2 \end{array} \right. \quad (15)$$

and $E_{\mathbf{s}}$ given by Eq.(3), with \mathbf{s}_{ij} instead of \mathbf{r}_{ij} .

These results may be applied directly in computer simulations, nevertheless the efficiency suffers from the lack of reduction in one particle summations, as for Coulomb potentials in quasi-two dimensional systems, because of the complicated dependence on z_{ij} . For molecular dynamics implementations, the forces acting on particles can easily be obtained with computations of the derivatives of the interaction potential.

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